SB 521 Research Project Review
Executive Summary
Review of Volumes I - V
"Health and Environmental Assessment of MTBE"
Office of Mobile Sources
Office of Air and Radiation, USEPA

February 5, 1999

Air Quality Benefits

The use of reformulated gasoline (RFG) has resulted in significant reductions in volatile organic compounds (VOC), nitrogen oxides (NOx) and toxics, such as benzene, when compared to emissions from the use of conventional gasoline. The federal RFG program reduces annual VOC emissions by over 15%, NOx by 2-6%, and air toxics by 15-30% in the ambient air in areas where RFG is used. The use of California Phase 2 reformulated gasoline (CaRFG2) has also substantially reduced levels of VOCs and NOx in California, and like RFG, CaRFG2 has reduced benzene levels by 40% or more.

The University of California (UC) report, Volume III-1 concludes that "MTBE and other oxygenates have been found to have no significant effect on exhaust emissions of CO, NOx, and VOC from advanced technology vehicles using reformulated fuel" and that "there is no significant additional air quality benefit to the use of oxygenates such as MTBE in reformulated gasoline, relative to non-oxygenated CaRFG2 formulations." Although it is possible to produce non-oxygenated fuel that meets California Phase 2 reformulated gasoline (CaRFG2) requirements, USEPA is concerned that readers of the report should also be made aware of the role that MTBE currently plays in meeting reformulated gasoline requirements. Specifically, the use of oxygenates directly reduces carbon monoxide (CO) and toxics emissions. Further, the addition of MTBE to gasoline also dilutes other fuel components and thereby reduces sulfur, olefin, aromatic, and benzene levels, regardless of whether the fuel is used in advanced or older technology vehicles. And, it is well established that these fuel component reductions in turn will reduce emissions of VOCs, NOx and toxics. The removal of MTBE (or a reduction in its concentration) would result in increases in some or all of these fuel components in gasoline, or would require substantial refinery capital investments to continue to meet CaRFG2 requirements. Finally, the authors find a significant increase in formaldehyde emissions due to MTBE. However, USEPA believes that the use of oxygenates results in significant reductions in other air toxics including benzene, acetaldehyde, and 1,3-butadiene. More specific comments on this are included in USEPA's comments on Volume III-1.

It is particularly important to note that the CaRFG2 fuel analyzed by UC in Volume III-1 <u>is not</u> the same fuel used for the cost-benefit analysis in Volume V of the UC report. As discussed in USEPA's comments on Volume V, the fuel described as "non-oxygenated CaRFG2" fuel in Volume V would not meet CaRFG2 emissions reductions requirements. USEPA believes

this is a critical disconnect between Volumes III and V of the UC analysis. USEPA is particularly troubled with the report's assumption in Volume V that "To produce non-oxygenated CaRFG2, the most likely replacement of MTBE is toluene." Using toluene instead of MTBE would increase the aromatic content and result in higher toxic and benzene emissions. Further analysis to support this conclusion is included in USEPA's comments on Volume V-7.

Water Quality

The UC report states that "There are significant risks and costs associated with water contamination due to the use of MTBE. MTBE is highly soluble in water and will transfer readily to groundwater from gasoline leaking from underground storage tanks, pipelines and other components of the gasoline distribution system."

In USEPA's view, water contamination by gasoline compounds is never acceptable. As a statement used in both the Executive Summary and the Fact Sheet, we believe that this point lacks adequate context. It should be noted that, as of November 23rd, California has sampled 894 public water systems that collectively serve approximately 27.5 million people in the state, and 35 of the systems (3.9%) have shown detectable levels of MTBE, nearly all with concentrations below 20 micrograms per liter. Even so, in presenting such facts, USEPA does not mean to minimize our recognition of the impacts from MTBE which have resulted in the closure and on-going remediation of drinking water wells in Santa Monica, Santa Clara Valley, and South Lake Tahoe, California. Rather, the inclusion of such occurrence data as additional context is intended to emphasize that there is still much to be learned about the potential for current and future impact to ground water resources which may result from the use of MTBE. EPA is in the process of collecting and evaluating necessary data which may help to place drinking water impacts, air quality benefits, and costs into perspective. These efforts include work being undertaken by the Office of Research and Development on health effects and remediation options; research efforts being undertaken at the Port Hueneme petroleum hydrocarbon remediation demonstration site; work being done on all aspects of MTBE cleanup and response, in conjunction with the Los Angeles Regional Water Quality Control Board, in Santa Monica CA; and USEPA participation in the State of California MTBE groundwater vulnerability analysis project.

Health Effects

USEPA agrees with the UC report's overall conclusion that "the scientific understanding of the mechanisms by which MTBE causes cancer in laboratory animals is nascent, and therefore uncertainties remain about the nature and extent of risk to humans, especially for exposure to doses lower than those used in animal studies." The UC report further cites the 1997 "Interagency Assessment of Oxygenated Fuels" which was released by the White House's Office of Science and Technology Policy and stated that "There is sufficient evidence to indicate that MTBE is an animal carcinogen and to regard MTBE as having a human hazard potential.

Estimates of cancer potency derived from MTBE animal studies as well as estimates of human exposure to MTBE have large uncertainties and caution is required in their use." This is consistent with USEPA's view at this time.

Recent decisions from other scientific groups also express the current carcinogenic uncertainty associated with human exposure to MTBE. The International Agency for Research on Cancer (IARC), which operates under the World Health Organization (WHO), has concluded that MTBE is currently "not classifiable as a human carcinogen" in a full report to be released in Spring 1999. And, this past December, the National Toxicology Program (NTP) Board of Scientific Counselors, voted against listing MTBE in their 9th Report on Carcinogens (RoC), for chemicals and substances known to be human carcinogens or which may reasonably be anticipated to be human carcinogens. Finally, under the Safe Drinking Water and Toxic Enforcement Act (Prop 65), California EPA's Office of Environmental Health Hazard Assessment recently made the decision not to list MTBE on "a list of chemicals that are known to the State of California to cause cancer, birth defects or other reproductive harm." A majority of the committee members indicated that, in their opinion, results of animal studies were too weak to qualify for listing under Proposition 65 at this time.

In an effort to better understand the health risks associated with exposure to conventional gasoline and oxygenated gasolines, USEPA has recently finalized health effects testing requirements that industry will complete over the next two to five years. The tests involve short term and long term animal inhalation studies, including comparative carcinogenicity tests on conventional gasoline and MTBE gasoline to better estimate their respective inhalation risk in humans.

Costs/Benefits

The UC report states that "Economic analysis of the benefits and costs associated with three gasoline formulations indicates that non-oxygenated gasoline achieves air quality benefits at the least cost, followed by CaRFG2 with ethanol. CaRFG2 with MTBE has the highest net annual cost due primarily to the costs of treating contaminated water supplies, higher fuel prices, and lower fuel efficiency."

USEPA does not agree with some of the methodology used in comparing the CaRFG2-MTBE, CaRFG2-Ethanol and non-oxy CaRFG2 fuel blends. Specifically, there appear to be serious cost-benefit inconsistencies associated with the idea of substituting toluene for MTBE, as well as the procedure for cost comparison of the three fuel blends in the categories of fuel price increases and water treatment costs.

Fuel Cost Estimates

In regard to fuel price increases, the report states that "To produce non-oxygenated CaRFG2, the most likely replacement of MTBE is toluene." This in fact could not happen. Using toluene instead of MTBE would increase aromatic content, increase the toxic and benzene

emissions of such a fuel and cause the fuel not to meet CaRFG2 requirements. Moreover, the non-oxygenated CaRFG2 fuel described in Volume V is not the same CaRFG2 fuel analyzed in Volume III's assessment of air quality benefits. Therefore, the report does not present a realistic assessment of the cost associated with a non-oxygenated replacement fuel that maintains the air quality benefits of CaRFG2.

The UC report also states that "The annual extra cost to California of using MTBE to meet CaRFG2 requirements, assuming an annual consumption of 13.5 billion gallons (Board of Equalization, 1998), is $278 to $973 million." In contrast, the costs of a non-oxygenated CaRFG2 fuel were quantified in a recent California Energy Commission (CEC) report "Supply and Cost Alternatives to MTBE in Gasoline" which stated that "If the scope of replacing MTBE were to be broadened to include the elimination of all oxygenates from gasoline, the cost impact for [California] consumers would be the greatest, regardless of the length of time allowed for the transition, ranging up to 8.8 cents per gallon in the intermediate term and 3.7 cents per gallon in the long term. On an annual basis these costs would amount to $1.3 billion and $580 million, respectively." USEPA believes that this analysis should be more fully considered and incorporated into the final version of the UC report.

Remediation Costs

USEPA does not agree with the methodology used for cost comparison in the category of water treatment costs. Specifically, USEPA believes the cost/benefit analysis section in Volume V inappropriately allocates to the CaRFG-MTBE fuel, remediation costs associated with past UST releases. The report states that "The groundwater remediation cost includes the legacy of older leaking USTs that stored gasoline with MTBE, which will cost from $320 to $1,030 million per year to remediate, relative to conventional gasoline leaks." USEPA agrees that remediation costs from USTs that stored gasoline containing MTBE can be higher than those that stored conventional gasoline. However, this comparison should not be used for the purposes of a cost-benefit analysis for future choices in gasoline formulation, since the remediation costs from USTs that previously stored gasoline containing MTBE are considered "sunk" costs (i.e., these costs would be equally incurred under each of the various fuel formulation options). Therefore, these remediation costs should have been assigned to all three fuel types (CaRFG2 non-oxygenated, CaRFG2 with ethanol, and CaRFG2 with MTBE) or removed from consideration altogether.

SB 521 Research Project Review

Review of Volume III-1
"Evaluation of Automotive MTBE Combustion Byproducts"
Office of Mobile Sources, USEPA
and
Paul Lemieux, National Risk Management Research Laboratory
Office of Research and Development, USEPA

Office of Mobile Sources

The use of reformulated gasoline (RFG) has resulted in significant reductions in volatile organic compounds (VOC), nitrogen oxides (NOx) and toxics, such as benzene, when compared to emissions from the use of conventional gasoline. The federal RFG program reduces annual VOC emissions by over 15%, NOx by 2-6%, and air toxics by 15-30% in the ambient air in areas where RFG is used. The use of California Phase 2 reformulated gasoline (CaRFG2) has also substantially reduced levels of VOCs and NOx in California, and like RFG, CaRFG2 has reduced benzene levels by 40% or more.

First, it is important to note that the CaRFG2 fuel analyzed by UC in Volume III-1 is not the same fuel used for the cost-benefit analysis in Volume V of the UC report. As discussed in USEPA's comments on Volume V, the fuel described as "non-oxygenated CaRFG2" fuel in Volume V would not meet CaRFG2 emission reduction requirements. USEPA believes this is a critical disconnect between Volumes III and V of the UC analysis.

The University of California (UC) report, Volume III-1 concludes that "MTBE and other oxygenates have been found to have no significant effect on exhaust emissions of CO, NOx, and VOC from advanced technology vehicles using reformulated fuel" and that "there is no significant additional air quality benefit to the use of oxygenates such as MTBE in reformulated gasoline, relative to non-oxygenated CaRFG2 formulations." Although it is possible to produce non-oxygenated fuel that meets California Phase 2 reformulated gasoline (CaRFG2) requirements, USEPA is concerned that readers of the report should also be made aware of the role that MTBE currently plays in meeting reformulated gasoline requirements. Specifically, the use of oxygenates directly reduces carbon monoxide (CO) and toxics emissions. Further, the addition of MTBE to gasoline also dilutes other fuel components and thereby reduces sulfur, olefin, aromatic, and benzene levels, regardless of whether the fuel is used in advanced or older technology vehicles. And, it is well established that these fuel component reductions in turn will reduce emissions of VOCs, NOx and toxics. The removal of MTBE (or a reduction in its concentration) would result in increases in some or all of these fuel components in gasoline, or would require substantial refinery capital investments to continue to meet CaRFG2 requirements.

USEPA notes that the impact of removing oxygenates is not identical for CaRFG2 and federal RFG. Federal RFG is subject to fewer caps on specific properties than CaRFG2 and is therefore likely to show greater emissions impacts from the removal of oxygenates. Most refiners are producing federal RFG with far less toxic air pollutant emissions than required by federal

regulations. Some refiners are also producing RFG that exceeds the VOC or NOx reduction requirements. These refiners could respond to a reduction in MTBE levels by allowing sulfur, olefin, and/or aromatic levels to increase (due to reduced dilution and, in the case of aromatics, to make up for the loss in octane). The resulting gasoline would emit more VOC, NOx, and toxic air pollutants but could still meet the federal RFG requirements.

The California Energy Commission (CEC) analysis, completed in October, 1998, indicated that refiners would use approximately 1.8 wt% oxygen to meet CaRFG2 requirements, even without an oxygen mandate. A similar analysis, for the Northeastern United States, by the Department of Energy, concluded that refiners would use about 75% of the MTBE they currently use to produce Federal RFG, even if the oxygen mandate did not exist. Refiners utilize the oxygenate to displace other fuel components such as sulfur, olefins, and aromatics to help meet the VOC, NOx, and toxics reductions requirements, and to restore octane that is lost by reducing these other fuel components.

Regarding direct benefit from the use of oxygenates, particularly for older vehicles, the June, 1997 Office of Science and Technology Policy assessment of the use of oxygenates in the winter oxygenated fuels program concluded that "analyses of ambient CO measurements in some cities with winter oxygenated gasoline programs find a reduction in ambient CO concentrations of about 10%." Regarding toxic effects, the UC report on MTBE Combustion Byproducts focuses on the set of Auto/Oil dynamometer studies. The studies relevant to toxic effects due to changes in MTBE content are summarized individually in Auto/Oil Technical Bulletins 5, 6, and 17, and then as a whole in the Auto/Oil Final Report. These studies comprise the bulk of the toxics data used in the development of the USEPA's Complex Model, which represents Tier 0 and Tier 1 vehicles. According to the Complex Model, the addition of 11 vol% MTBE to California RFG will produce a 7% reduction in benzene, a 6% reduction in acetaldehyde, an 11% increase in formaldehyde, and a 5% decrease in 1,3-butadiene. The increase in formaldehyde is consistent with the statements made by the authors of the UC report, and the fact that it is the largest change for these four toxic compounds lends credence to the observation that only formaldehyde increases were found to be statistically significant. However, the USEPA does not believe that the decreases in other toxic compounds should be ignored on the basis of their statistical significance. In fact, the relationships in the Complex Model were based on regression analyses that ensured a minimum level of significance. On this basis, then, the USEPA believes that the reductions in benzene, acetaldehyde, and 1,3-butadiene predicted by the Complex Model are just as valid as the predicted increase in formaldehyde emissions.

Paul Lemieux, USEPA's Office of Research and Development (ORD)

From a technical standpoint, the study "Evaluation of Automotive MTBE Combustion Byproducts" section (volume III - 1) was well done and informative. However, this does not suggest concurrence on the overall conclusions, as has already been discussed in earlier comments. More specifically, there are several items that I believe should be addressed in order to improve the scientific basis for the report.

Editorial comments

- page 8 line 3 -- word is missing -- maybe "The authors speculate that..."?

- NOx should have the x subscripted

- The figures and tables should be inserted into the text instead of at the end.

General Comments

- The authors did not adequately make a distinction where in the system the combustion by-products are formed. The issue of product of incomplete combustion (PIC) formation in the automotive combustion chamber at elevated pressures vs PIC formation in the exhaust manifold at atmospheric pressure is critical. Most of the laboratory data presented, especially the authors' own data, were all taken at atmospheric pressure. This topic merits a subsection to discuss the issues of formation at high vs low pressure. The literature survey that was presented was not organized in such a way to describe some of the influences of pressure and temperature on the MTBE destruction/PIC formation reactions. A Figure similar to Figs 1 and 2 which describes the kinetic pathways at elevated pressure would be very useful.

- The measurement methodologies that the authors used for their own experiments are not sufficiently sensitive to definitively allow conclusions such as "no TBF formation is observed". FTIR has fairly poor sensitivity in the best of circumstances. Method detection limits on the order of 1-10 ppmv are insufficient to adequately measure any but the highest concentration PCS that are formed. It is recommended that the authors address this measurement limitation in the way they present the data. On all of their reported data where non detects occur, It is recommended that they calculate method detection limits (MDLs) for those compounds and include in their tables "< XXX" where XXX is the MDL. On the bag samples that were reported from the dyno tests in terms of mg/mi -- what concentrations in the gas phase do those translate into? Are they sufficiently high that your 1 ppm MDL for the FTIR could state definitively whether compounds that might have been found in the bag samples would not be found from the lab experiments?

Specific Comments

Page ii: are ppb and ppm on a volume or mass basis?

Page 14 ¶ 3: back to the ppm question; how do you define ppm for gasoline which really has no molecular weight? Is this a true ppmv or a ppm mass (mg/m3) or is it an equivalent ppm methane or propane?

Page 15 ¶ 3: what numeric value constitutes "nearly complete destruction" of MTBE? Is this based on an MDL limitation or were you able to measure 90% or 99% or whatever destruction? How does the MDL relate to minimum and maximum measurable destruction?

Page 15 ¶4: When you say "No TBF formation is observed", at what level is this true? This relates back to the MDL issues.

Page 14 ¶5: Same thing with "no methanol is produced". At what levels?

Page 34: are the mg/L emissions based on mg/L gas phase or mg/L fuel?

SB 521 Research Project Review

Review of Volumes I, II, & III
"Health and Environmental Assessment of MTBE"
Office of Science and Technology
Office of Water, USEPA
and USEPA Region 9

Office of Water

Overall, the authors have reviewed a large body of material and placed it in a logical order and are to be commended. We would also appreciate receiving a copy of the final document when the review process has been completed. In this review, the Health and Environmental Criteria Division (HECD) has limited its comments to the effects of MTBE on human health and the environment. We did not review the health and environmental effects of the other chemicals, e.g., TAME, the air quality or the exposure and treatment sections.

Specific comments

Volume II - Human Health Effects

1. Although a minor comment from the scientific aspect, the document could benefit from some technical editing. For example, on p. xviii, the ref is USEPA, 1977a; on p. 10 ref is CARB 1991a (no comma). Same in several other places. Other problems include such things as Anderson et al. (No year given) on p. 61, 3rd para.
2. On p. xviii, ref is USEPA, 1997a, there is no USEPA, 1997a in ref list (see p. 207).
3. p. 22, 2nd para - Young et al., 1996 and Dale et al. (Need a year to be given) are cited. The Young paper was published in a peer-reviewed journal, while the Dale data was presented at an AWWA meeting. Do you make any distinction between published and unpublished data. There is have no problem with using unpublished data, but it should be identified as such and a critical review of the data done prior to using such data.
4. p. 23, l. 2-3 - "Water spiked with MTBE ... Table 1 presents the data as ranges ..." Table 1 in Vol. II is "Estimation of Chronic Daily Doses ... (It does not appear that Table 1 of the paragraph is Table 1 OG Vol. II. The Table 1 means Table 1 of what?) In addition, this paragraph is not referenced. If this is supposed to justify the statement in the fourth paragraph of p. viii of the Executive Summary which states "the taste and odor thresholds for MTBE range from 2.5 ppb to 680 ppb and 2 ppb to 190 ppb, respectively", then you need a much better explanation and reference.
5. On p. 56, Section 5.1.1 should make it clear at the beginning that the MTBE in these studies was part of exposure to gasoline containing MTBE.

6. Carcinogenicity studies, p. 106-108 - It should be stated that the vehicle was an oil (olive oil) and that vehicle effects have been reported, e.g., vinylidene chloride in oil or water vehicles. In addition, it should be mentioned that an NRC panel (NRC, 1996; Toxicological and performance aspects of oxygenated motor vehicle fuels) recommended an detailed independent review of the data. This report was cited by NSTC (1997).

Volume III - Air Quality and Ecological Effects

In addition to the ecological effects information presented in Volume III, new aquatic life toxicity data for MTBE is becoming available. Seventeen acute and chronic exposure tests with 8 freshwater and 7 marine species have been conducted over the past year under a major research effort initiated by the American Petroleum Institute (API). These newly generated data have undergone at least one level of quality assurance review. The preliminary results of this research effort were summarized in a poster presentation at the 19th Annual Meeting of the Society of Environmental Toxicology and Chemistry (SETAC). A copy of this poster presentation is attached.

USEPA Region 9

Taste and Odor

UC did an excellent job of summarizing the laboratory studies that document the taste and odor threshold for MTBE in drinking water. Those studies suggest that MTBE can be tasted or smelled at very low levels and some health advisories or goals have been set based on those lab studies. However, MTBE contamination in water supplies has not typically been discovered as a result of taste or odor complaint from water users. Instead, it has most often been discovered during investigation of a gas station leak or as a result of routine sampling of a drinking water well (this was the case in Santa Monica). The UC report should discuss this issue.

SB 521 Research Project Review
Review of Water Treatment Sections of Volume V
Office of Ground Water and Drinking Water
and USEPA Region 9

Office of Ground Water and Drinking Water

Title: ***MTBE: Evaluation of Management Options for Water Supply and Ecosystem Impacts***

Water Treatment Section (Pages 18-21)

The water treatment section is very limited. The chapter tries to cover too much material in too short a space. The technology discussions should be placed in the treatment sections. The chapter limits itself to two paragraphs per technology. This is insufficient due to the technical complexities in discussing water treatment technologies.

Only a cursory discussion of the performance and cost of the technologies is made. It mostly references an ACWA report and a Malcolm Pirnie report which may be the same publication. It is difficult to judge the ACWA reference because it has yet to be released to the public. Therefore, since no treatment information is given in the chapter, it is impossible to judge the accuracy of the chapter's conclusions.

There was one technical mistake in the text. The last sentence of the "Adsorption" section states "Synthetic resins have shown good TDS removal in groundwater and are cheaper than Carbon adsorption because of resin's larger adsorption capacities." This is incorrect in two ways:

1) Carbonaceous adsorbents remove hydrophobic compounds, they do not remove TDS. Do the authors mean "MTBE" instead of "TDS"? Ion exchange resins remove TDS, but not nonionic organics such as MTBE. Ion exchange resins are inappropriate for MTBE removal.

2) Carbonaceous adsorbents do have a higher capacity than GAC for MTBE, but a number of references have shown that carbonaceous adsorbents are still more expensive than GAC for MTBE treatment because of high resin costs (Malley et al., 1993). Is there a more recent reference to support this statement?

Title: ***Cost and Performance Evaluation of Treatment Technologies for MTBE Contaminated Water***

This chapter references the MTBE Research Partnership report (1998) a great deal. Unfortunately, the report is not yet available to the public. The authors reference McKinnon and Dyksen (1984) early in the text, but they never compare their cost estimates to the actual costs found by McKinnon and Dyksen (1984). This would be a good verification of the cost model and its assumptions. The authors also reference the MTBE Research Partnership report (1998), but they do not compare results. For advanced oxidation, the chapter uses the MTBE Research Partnership (1998) cost numbers; however, no details are given, and the MTBE Research Partnership report (1998) is not yet available to the public. Overall, the final cost results in Table 12 for GAC look a little low. The advanced oxidation costs look high. Others have shown that advanced oxidation is the most cost effective technology, when compared to air stripping with off-gas treatment (Oxygenated Fuels Assoc./Malcolm Pirnie, 1997; American Petroleum Institute, 1991). A more detailed comparison to previous work is needed.

Steam regeneration of GAC will not be effective. Even if the steam removes the MTBE, the other more strongly adsorbed contaminants/molecules, including natural organics, will remain

on the carbon, hence reducing the carbon's capacity for MTBE. This effect will only get worse with subsequent regenerations. Other processes such as a multiple hearth furnace will be required for regeneration (Adams, JAWWA, 1986; Cairo et al., JAWWA, 1982; Schuliger et al., AWWA proceedings, 1987).

The authors claim that there are no economies of scale beyond flow rates above 500 gpm. This is not true because it ignores staggered-bed starts and on-site regeneration facilities.

Most of the assumptions for cost constants are adequate. However, the variable O&M assumption are rough. This would make one technology more favorable than another without justification based on true performance. The membrane stripping O&M is likely to be higher than that indicated in the text. It does not account for inorganic fouling. GAC reactivation will probably need more than steam regeneration.

Title: ***Estimated Cost Associated with Biodegradation of MTBE***

The chapter needs to be expanded. Little information was given to allow for an adequate review. The pilot-scale trickling filter was composed of GAC, yet no mention was made about whether the MTBE adsorbed onto the carbon, or volatilized into the air. The actual data should be presented so that a more thorough review can be made.

Title: ***Reactivity and By-Products of Methyl Tertiary Butyl Ether Resulting from Water Treatment Processes***

General:

This manuscript comprises an overview of a research project studying the ability of both chlorination and the hydrogen peroxide/UV AOP (advanced oxidation process) to degrade methyl *tert*-butyl ether (MTBE) and daughter products from the initial MTBE degradation. The document contains an introductory section providing a very brief description of chlorination treatment and ultraviolet (UV) treatment, and a slightly longer review of AOPs and the H_2O_2/UV AOP in particular. This latter material also cited several relevant papers describing treatment of MTBE laden waters by ozonation and AOPs.

The bulk of the document was devoted to describing the experimental design and the results. Chlorination experiments were conducted in batch mode in pH-buffered (pH 4 and 7) Nanopure water spiked with MTBE. In short, no degradation of MTBE occurred via reaction with HOCl/OCl- in the system studied.

Control experiments to check for reaction between H_2O_2 and MTBE were also conducted in batch mode in pH-buffered (pH 7) Nanopure water spiked with MTBE. No degradation of MTBE was observed.

Experiments for UV-alone and H_2O_2/UV degradation of MTBE were performed in a flow-through reactor which acted as a modified CSTR. For these experiments MTBE was again spiked into pH-buffered (pH 6.5) Nanopure water. Experiments testing the ability of UV light irradiation alone to degrade MTBE indicated that no significant degradation took place in these clean water systems. In contrast, the H_2O_2/UV demonstrated the ability to degrade 99.9% of the MTBE in the experimental system. The authors found that *tert*-butyl formate (TBF) was the major degradation product, but found no other initial or secondary by-products. TBF was formed with an average yield of 27% (yield from MTBE). By addition of benzene in these systems, which served as a hydroxyl radical (OH) probe compound, the authors also measured rate constants for the reaction of OH with MTBE ($4.82[\pm1.28] \times 10^9$ $M^{-1}s^{-1}$) and OH with TBF ($1.19[\pm0.447] \times 10^9$ $M^{-1}s^{-1}$).

Comments:

The inclusion of the chlorination studies (i.e. degradation of MTBE by HOCl/OCl-) added little to the document. It is fairly well accepted that chlorination is an ineffective process for MTBE degradation at the conditions typically employed for drinking water treatment. The authors described the intended dosage of Cl_2 used in these studies, but they did not explicitly mention if they directly measured the actual dosage. Nonetheless, their results showing no discernable degradation is consistent with other reports.

In terms of the H_2O_2/UV studies, this document adds to the growing list of reports of MTBE treatment by AOPs. The common goal of all AOPs is to produce OH at high enough concentrations such that the pollutant can be degraded. To that extent, degradation of MTBE does not depend upon which AOP method (e.g. H_2O_2/UV, UV/O_3, H_2O_2/O_3, O_3/sonolysis, etc.,) is used to produce OH[1].

Therefore, the first major question is: Assuming OH reacts with MTBE (OH reacts with most anything), what is the reaction rate? The authors have made an attempt to measure this reaction rate by use of an OH probe compound. Their methods are correct, but their experimental data set is not very robust and they are forced to measure reaction rates from initial-rates data. Nonetheless, the rate constant they extract from their study ($k = 4.82[\pm1.28] \times 10^9$ $M^{-1}s^{-1}$) is reasonably close to the "accepted" value (measured directly) of 1.6×10^9 $M^{-1}s^{-1}$. The authors' experiments basically helps confirm that the already published rate constant is correct within an order of magnitude.

Given this rate constant, it possible to *a priori* calculate the rate of MTBE degradation by OH <u>if the concentration of OH is also known</u>. The concentration of OH will of course depend on the AOP chosen and furthermore on the properties of the water (temperature, pH, DOC concentration, alkalinity, turbidity, nature of the DOM, etc.,). This study limited itself to the H_2O_2/UV AOP in basically pure water (inorganic buffer added). The fact that they showed that

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[1] This is explicitly true only for homogeneous AOP processes such as those given as examples. This is in contrast to heterogeneous processes (e.g. UV/TiO_2, Fenton's processes, and processes using catalytic decomposition of H_2O_2 or O_3) which can produce OH at localized sites. This also does not take into consideration whether or not MTBE is degraded by other process factors such as reaction with O_3, H_2O_2, or degradation via direct sonolysis.

99.9% of MTBE could be degraded by H_2O_2/UV is an indication that they can produce OH in "clean" aqueous systems by this AOP (something that is already known), and with long enough reactions, MTBE can be degraded to a significant extent.

The more important question that this study does not address is: Can the H_2O_2/UV AOP degrade MTBE in natural waters where there are many other chemical species that can 1) scavenge OH hence decreasing OH concentration available for MTBE reaction, and 2) absorb the incident UV radiation thus decreasing the efficiency of cleavage of H_2O_2 to form OH?

The authors allude to these factors in their final section (*Opportunities for Further Research*), but the feasibility of the H_2O_2/UV AOP to degrade MTBE in natural waters is in fact the heart of the issue. Once again, this document does not address this issue.

One additional conclusion in this work is worth discussion. This work provides an [estimated][2] value for the reaction rate of OH and *tert*-butyl formate. To my knowledge, this value has not been reported previously. However, this value must be considered only an estimate (order of magnitude) because of the use of initial-rates data, the lack of mass balance in the formation of TBF from MTBE. In other words, the data-fitting scheme apparently did not fit the MTBE/TBF yield and the OH/TBF rate constant independently of each other (two parameters were fit per each data set).

Moreover, there is still the consideration that the sole pathway for TBF degradation is not direct reaction with OH. It was not clear if the authors checked for reaction between UV and TBF, H_2O_2 and TBF, and particularly the hydrolysis of TBF to form *tert*-butyl alcohol.

USEPA Region 9

Ground Water Treatment Levels (Volumes I and V)

The reports seem to imply that treatment of groundwater contaminated with MTBE will typically be required down to the secondary MCL level of 5 ppb. However, it is likely that there will be cases when contamination is not in close proximity to production wells, and treatment to another level may be more appropriate. Page 52 of the summary report states "In the event that water supplies become contaminated with ethanol, the available toxicological information does not support treating the water to the low levels required by MTBE." It is still not clear that the toxicological data supports treating MTBE down to low levels (5 ppb) either.

SB 521 Research Project Review

Review of Volume V-7

"An Integral Cost-benefit Analysis of Gasoline Formulations Meeting California Phase II Reformulated Gasoline Requirements"

Office of Mobile Sources

Office of Air and Radiation, USEPA

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[2] Reviewer's emphasis

USEPA does not agree with some of the methodology used in comparing the CaRFG2-MTBE, CaRFG2-Ethanol and non-oxy CaRFG2 fuel blends. Specifically, there appear to be serious cost-benefit inconsistencies associated with the idea of substituting toluene for MTBE, as well as the procedure for cost comparison of the three fuel blends in the categories of fuel price increases and water treatment costs.

Toluene Assumption

First, it is important to note that the CaRFG2 fuel analyzed by UC in Volume III-1 is not the same fuel used for the cost-benefit analysis in Volume V of the UC report. As discussed here, the fuel described as "non-oxygenated CaRFG2" fuel in Volume V would not meet CaRFG2 emissions reductions requirements. USEPA believes this is a critical disconnect between Volumes III and V of the UC analysis.

CaRFG2 with toluene displacing MTBE would not comply with current regulations; such a fuel would not meet California's aromatics cap. As a result, equal air quality benefits cannot be assumed for the three fuel options considered in the cost-benefit analysis. Specific comments on the air quality benefits conclusions are included under USEPA's comments on Volume III-1.

The UC report assumes that to produce non-oxygenated RFG, the most likely replacement of MTBE is the aromatic compound toluene, and estimates the direct costs of non-oxygenated CaRFG2 based on this assumption. This assumption may be based on Auto/Oil tests with two fuels, reformulated gasoline C2 with MTBE and a reformulated gasoline C1 without oxygenate. The properties of these two fuels are:

	C2 (oxy)	C1 (non-oxy)	
Aromatics Vol.%	25.4		22.7
Olefins Vol. %	4.1		4.6
MTBE Vol. %	11.2[3]	0	
Benzene, Vol. %[4]	0.93		0.94
Sulfur, ppm	31		38
RVP ,psi	6.8		6.9
T10	142		142
T50	202		208
T90	293		297
Net HV, BTU/lb	18,091	18,596	
API Gravity	59.9		62.2

[3]Equivalent to 2.05% oxygen

[4]Labeled in Auto/Oil bulletin no. 17 as weight percent rather than volume percent. Believed to be a misprint based on fuel analyses contained in other Auto/Oil bulletins.

Of particular importance in this context is the aromatic content of the fuels. The aromatic content of C1, the non-oxygenated fuel, is lower than that of the oxygenated fuel. While these two fuels may produce similar emissions and, thus, similar air quality benefits, this behavior cannot be extended to the scenario considered in the UC cost-benefit analysis.

Because the UC report assumes substitution of the aromatic toluene for MTBE, the aromatic content of the non-oxygenated fuel under this scenario would be higher, not lower than CaRFG2 with MTBE. The effect of aromatic content on toxic emissions is well documented. The Auto/Oil final report notes that of the fuel properties tested, aromatic levels had the largest effect on total toxics, largely due to its effect on exhaust benzene emissions. As aromatic content increases, total toxics and benzene emissions are expected to increase.

USEPA's complex model or the California predictive model can be used to quantitatively demonstrate the effect of substituting aromatics for MTBE. For instance, the federal Phase II RFG complex model predicts an exhaust benzene emission level of 33.6 mg/mi and a total toxics emission level of 59.3 mg/mi for the C2 fuel. This fuel contains 11.2 volume percent MTBE, and 25.4 volume percent aromatics. If MTBE were replaced with an equal volume of toluene, the aromatics content would increase to 36.6 percent. This volume percent exceeds the California cap on aromatics of 30 percent.

Assuming that MTBE were replaced with aromatics up to 30 percent, that the remainder of the lost volume was made up with saturates, and that other properties do not change, complex model emissions for the resultant fuel are 41.0 mg/mi for exhaust benzene, and 66.1 mg/mi for total toxics. Exhaust benzene and total toxics emissions from this "MTBE replaced with toluene" fuel are estimated to be about 22 percent and 11 percent higher respectively than emissions from the C2 fuel. Phase II RFG complex model emissions for the C1 fuel, the non-oxygenated "RFG-like" fuel, are 36.2 mg/mi for exhaust benzene, and 62.7 mg/mi for total toxics. While these emission levels are higher than the levels for the C2 fuel, they are lower than the emissions levels predicted for the "MTBE replaced with toluene" fuel.

Thus, while the model predicts some differences in toxics emissions between the C2 fuel and the C1 fuel, the differences are smaller than the differences between the C2 fuel and the "MTBE replaced with toluene" fuel. This demonstrates that the Auto/Oil results do not support the assumption made in the cost-benefit analysis of equivalent air quality benefits in conjunction with substitution of toluene for MTBE.

In summary, if the equal air quality benefit assumption is to be kept for all three options, CaRFG2-MTBE, CaRFG2-Ethanol, and non-oxy CaRFG2, then the cost estimates based on substitution of toluene for MTBE need to be reconsidered. Alternatively, if the assumption that toluene will be substituted for MTBE is to be kept, then the assumption of equal air quality benefits needs to be reconsidered. Furthermore, the extent to which toluene can be substituted for MTBE is constrained by California RFG standards, such as the need to comply with a flat aromatics limit (25 percent volume), an averaging limit (22 percent with a cap of 30 percent), or an alternate limit subject to the cap which refiners determine with the Predictive Model. A 1996

API/NPRA survey of refining operations for the period from May 1, 1996-August 31, 1996 found average aromatic levels of 23.0, 23.5 and 22.8 volume percent for regular, mid, and premium reformulated gasolines produced in ten California refineries. They also found average levels of oxygen of 2.0 to 2.2 percent by weight, equivalent to about 11 percent MTBE by volume. While these numbers are aggregate averages, they do illustrate that it is unlikely that MTBE could be totally displaced by toluene in California consistent with current regulations.

Fuel Cost Estimates

In regard to fuel price increases, the report states that "To produce non-oxygenated CaRFG2, the most likely replacement of MTBE is toluene." This in fact could not happen. Using toluene instead of MTBE would increase aromatic content, increase the toxic and benzene emissions of such a fuel and cause the fuel not to meet CaRFG2 requirements. Moreover, the non-oxygenated CaRFG2 fuel described in Volume V is not the same CaRFG2 fuel analyzed in Volume III's assessment of air quality benefits. Therefore, the report does not present a realistic assessment of the cost associated with a non-oxygenated replacement fuel that maintains the air quality benefits of CaRFG2.

The UC report also states that "The annual extra cost to California of using MTBE to meet CaRFG2 requirements, assuming an annual consumption of 13.5 billion gallons (Board of Equalization, 1998), is $278 to $973 million." In contrast, the costs of a non-oxygenated CaRFG2 fuel were quantified in a recent California Energy Commission (CEC) report "Supply and Cost Alternatives to MTBE in Gasoline" which stated that "If the scope of replacing MTBE were to be broadened to include the elimination of all oxygenates from gasoline, the cost impact for [California] consumers would be the greatest, regardless of the length of time allowed for the transition, ranging up to 8.8 cents per gallon in the intermediate term and 3.7 cents per gallon in the long term. On an annual basis these costs would amount to $1.3 billion and $580 million, respectively." USEPA believes that this analysis should be more fully considered and incorporated into the final version of the UC report.

Remediation Costs

USEPA does not agree with the methodology used for cost comparison in the category of water treatment costs. Specifically, USEPA believes the analysis inappropriately allocates to the CaRFG-MTBE fuel, remediation costs associated with past UST releases. The report states that "The groundwater remediation cost includes the legacy of older leaking USTs that stored gasoline with MTBE, which will cost from $320 to $1,030 million per year to remediate, relative to conventional gasoline leaks." USEPA agrees that remediation costs from USTs that stored gasoline containing MTBE can be higher than those that stored conventional gasoline. However, this comparison should not be used for the purposes of a cost-benefit analysis for future choices in gasoline formulation, since the remediation costs from USTs that previously stored gasoline containing MTBE are considered "sunk" costs (i.e., these costs would be equally incurred under each of the various fuel formulation options). Therefore, these remediation costs should have been assigned to all three fuel types (CaRFG2 non-oxygenated, CaRFG2 with ethanol, and CaRFG2 with MTBE) or removed from consideration altogether.